REMARKS

STATUS OF THE CLAIMS

Claims 1, 4-7 and 9-13 are pending in the application.

Claims 2, 3 and 8 have been cancelled.

Claim 12 has been withdrawn.

Claim 1 has been amended.

Claim 13 is a new claim that has been added.

Claim 4 and 7 were previously presented.

Claims 5, 6, and 9-11 are original claims.

RESPONSE TO REJECTION UNDER 35 U.S.C. § 112

Claims 1 and 4-12 were rejected under 35 U.S.C. 112 first paragraph as failing to comply with the written description requirement. In particular, the Examiner objected to the description of aqueous composition 2 set forth in claim 1. Claim 1 has been amended to describe aqueous composition 2 which is fully supported in the specification on page 5, lines 3-8. As noted by the Examiner on page 3, of the office action second full paragraph, component A, the epoxy resin is mixed with water to form an epoxy resin dispersion and components B-D are mixed with the dispersion to form aqueous composition 2 having a solids content of 30% to 60%. This amendment to claim 1 obviates the '112 rejection. Claims 4-7 and 9-12 are directly dependent on claim 1 and the rejection of these claims is also obviated by this amendment. Claim 12 has been withdrawn from consideration and claim 8 has been cancelled.

Claim 8 was rejected under the second par. of 35 U.S.C 112 as being indefinite since the term "consists" was used in Claim 1 on which Claim 8 was dependent upon on the basis that the organo metallic compounds set forth in Claim 8 could not be included in the aqueous compositions 1 and 2. Claim 8 has been cancelled and new independent Claim 13 has been added wherein the organo metallic compounds are included in aqueous compositions 1 and 2. New Claim 13

should be allowable since it obviates the rejection raised under '112 concerning Claim 8.

RESPONSE TO OBVIOUSNESS REJECTION UNDER 35 U.S.C. § 103(A)--JP '723 (JP 11-162 723) IN VIEW OF EUROPE 059 (EP 717059) AND OPTIONALLY YOUNG (US 5,550,462) OF CLAIMS 1, 4-7 & 9-11

(I)   Examiner' Comments

In the office action, the Examiner asserted that Claims 1, 4-7, and 9-11 were considered obvious under 35 U.S.C. § 103(a) in view of JP 11-162723 (*hereinafter* "JP 723"), and EP Patent Application EP 0717,059 (*hereinafter* "EP 059"), and optionally, U.S. Patent No. 5,550,462 to Young, *et al.* (*hereinafter* "Young").

JP 723 was held to be directed to manufacturing a core for a motor or transformer and disclosed an aqueous compositions comprising 100 parts epoxy resin based on bisphenol-A-type, 1-40 parts hardening agent comprising latent curing agents, such as, dicyandiamide and phenol resin, water, and additives such as silica, pigments, "membrane formation assistant" and "dispersibility improver" and drying the coated steel sheets at elevated temperatures and applying heat and pressure thereby laminating/bonding the sheets together.

The JP 723 epoxy resin was held to read on part A of Claim 1, the dicyandiamide reads on part B of Claim 1, the phenol resin reads on part C of Claim 1, and the water reads on part E of Claim 1. As to part D of Claim 1, the Examiner stated that EP 059 suggests using a solvent. As to 50-200 parts of water set forth in Claim 1, it would have obvious to determine that amount of water without undue experimentation in view of the teachings of JP 723. The Examiner further stated that the use of "consists" fails to exclude the use of a phenol resin as an additional curing agent because the term "additives" in claim 1 is sufficiently broad to read on phenol resin.

(II)   APPLICANTS' RESPONSE TO EXAMINER'S COMMENTS

It is very clear that JP 723 requires the addition of a phenol resin as a curing agent for the epoxy coating composition used in the JP 723 process as set forth in par. [0014-0016] of the machine translation. Applicants do not use a phenol resin in

the coating composition used in the claimed process. The claims describing the aqueous coating composition used in the process use the term "consists of" which clearly excludes the presence of a phenol resin as required by JP 723. The Examiner has taken the position that the term "additive" used in Applicants' claims is sufficiently broad to cover phenol resins and has cited the following hodge podge of unrelated references to support his theory. Gunasekaran et al. U.S. 6,548,189 directed to epoxy adhesives was cited which states that an additive can be a curing agent among other things such as, bonding enhancers, hardeners, flexiblilizers and tackifiers. Yamaji et al. U.S. 6,569,513 directed to a prepreg and process for manufacturing the same states that additives can be curing agents, curing catalysts, filler, surfactant silane coupling agent and the like. JP 02124927 directed to a molding composition was cited and states that additives can be a crosslinking agent, a curing agent, a curing accelerator, a filler, a release agent, a coloring material and a coupling agent and goes further to state the phenol resin is a crosslinking agent which apparently contradicts the Examiner's position that phenol is other than a crosslinking agent. Lastly, JP 54097699 directed to accelerate the curing of an epoxy resin to improve thermal aging was cited which is truly unrelated since it teaches the addition of a reaction product of a phenol and a polyisocyanate to an epoxy resin.

To begin with, in the specification page 4, lines 22-26, Applicants clearly point out what they consider to be additives and a phenol resin is not included. Based on that alone, it is improper for the Examiner to put his own spin on the term and take the position that additive covers a phenol resin which it clearly does not. As the Examiner well knows, patents and published patent applications are not scientific documents and often contain jargon and terminology that is not entirely accurate at times just plain wrong. Certainly, the above references cited do not clearly point out what is meant by the term "additive" as it related to epoxy coating compositions. From the above cited collection of references, additives can be crosslinking agents which is clearly inaccurate to surfactant coupling agents.

When faced with such a situation, one must look to an established scientific reference, in this case Ullmann's Encyclopedia of Industrial Chemistry which is well know and well accepted in the coatings industry. Vol 18, pages 408, 409, 418 and 465-472 are attached hereto as Exhibit 1 (*hereinafter* referred to a "Ullmann").

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Applicants have highlighted relevant sections on Page 465 and quote from the same page as follows:

> **5. Paint Additives**
> In *addition* to *resins*, solvents, and pigments, paints also contain *additives*. The additive content is typically between *0.01 and 1%*. Paint additives are used to prevent defects in the coating (e.g., foam bubbles, poor leveling, flocculation, sedimentation) or to impart specific properties to the paint (e.g., better slip, flame retardance, UV stability) that are otherwise difficult to achieve.
>
> ...　　　　　　...　　　　　　...
>
> Additives may be classified in the following groups:
> 1) Defoamers
> 2) Wetting and dispersing additives
> 3) Surface additives
> 4) Rheology additives
> 5) Driers and catalysts
> 6) Preservatives
> 7) Light stabilizers
> 8) Corrosion inhibitors

According to Ullmann, additives are added **in addition** to resins to create compositions. In other words, additives are **NOT** resins. Phenol resin is a resin. Therefore, phenol resin is NOT an "additive," as interpreted by the pertinent art. Secondly, according to Ullmann, additives are used generally in the amount of 0.01% to 1%. JP 723 uses its phenolic resin in the amount from 0.3% to 28% according to the Examiner's calculations in a previous office action.

Further, Ullmann, page 408, par. 2.10.2, discusses curing agents for epoxy resins and Table 2.6 lists phenolic resin as a curing agent for epoxy resins. Page 409, teaches that phenolic resins react with high molecular weight epoxy resins. Page 419 teaches the use of phenolic resins for coatings. Clearly, Ullmann teaches that phenolic resin are curing agents for epoxy resins and not additives as alleged by the Examiner.

Based on the above discussion, the rejection based on JP 732 can not stand and must be withdrawn. Applicants' have defined the components of the aqueous composition used in the process by the term "consists of" which signifies a closed system of components used for the aqueous composition which clearly excludes phenolic resins that are required by JP 732 and are not included in the term "additive" as set forth in the claims. EP 059 only discloses that solvents can be used in epoxy resin coatings but is not directed to Applicants' process for the production of

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electrical steel sheet core for use in electrical equipment. Young shows stable epoxy resin dispersions that contain micronized dicyamide but again not directed to Applicants' claimed process.

In regard to the rejection of Claims 4-7 and 9-11 which are dependent on Claim 1 and recite even further limitations to Claim 1, Applicants rely upon the arguments presented above to rebut the Examiner's rejection that these claims are obvious and therefore, unpatentable over JP 723 in view of EP 059 and optionally, in view of Young.

Applicants respectfully submit that NOT all elements of Claim 1 are disclosed by the combined references JP 723, EP 059 and Young. Therefore, Claim 1 and by extension, its dependent claims are patentable and not obvious under 35 U.S.C. § 103(a).

RESPONSE TO REJECTION UNDER 35 U.S.C. § 103(A) OF CLAIM 8

Claim 8 was rejected under 35 U.S.C. § 103(a) as being unpatentable over JP 723 in view of EP 059 and optionally, in view of Young and further in view of Stark (U.S. Patent No. 4,307,212) or Kohn, *et al.* (U.S. Patent No. 2,962,410).

Claim 8 has been canceled and replace with Claim 13 to avoid the '112 rejection previously discussed. Claim 13 is directed to the process as set forth in Claim 1 wherein the aqueous compositions 1 and 2 each contain ortho-titanic or –zirconic acid esters. Applicants rely upon the arguments presented above to rebut the Examiner's assertion that Claim 8 which now has been replaced by Claim 13 is unpatentable over the above-cited references. Further, neither Stark nor Kohn are directed to Applicants' claimed process for the production of electrical steel sheet cores for use in electrical equipment but merely show curable epoxy resin compositions. There is no disclosure or suggestion is either Stark or Kohn that these esters can be used in Applicants' claimed process.

CONCLUSION

In view of the above remarks, Applicants respectfully submit that stated grounds of rejection have been properly traversed, accommodated, or rendered moot and that a complete response has been made to the Final Office Action mailed on December 13, 2007. Therefore, Applicants believe that the Application stands in condition for allowance with withdrawal of all grounds of rejection. A Notice of Allowance is respectfully solicited.

If the Examiner has questions regarding the Application or the contents of this Response, the Examiner is invited to contact the undersigned at the number provided.

RESPECTFULLY SUBMITTED,

DATED: March 7, 2008

BY: _____

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Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 18:
Nucleic acids to Parasympatholytics and
Parasympathomimetics

Editors: Barbara Elvers, Stephen Hawkins, Gail Schulz

VCH

1991

epichlorohydrin (diglycidyl ethers of butanediol, polypropylene glycol etc., → Epoxy Resins, A9, p. 552) are also used as reactive plasticizers. Polyglycidyl ethers (e.g., of sorbitol and pentaerythritol) are commercially available. They have a higher viscosity than the aliphatic mono- and diglycidyl ethers. They show good solvent resistance when cured with cycloaliphatic amines. Such resins are also cured with carboxy-functional polyesters, polyacrylates, or polyanhydrides to give coatings with good weather resistance.

Aliphatic epoxy resins generally have higher color stability and reactivity than aromatic epoxy resins, but their resistance to aqueous acid solutions is much lower.

Cycloaliphatic Epoxy Resins. Cycloaliphatic epoxy resins are produced by oxidizing olefins with peracids (→ Epoxy Resins, A9, p. 553). They are of only minor importance in surface coatings. They are cured with anhydrides, carboxy-functional substances, or Lewis acids at 150–200 °C. Ultraviolet curing with triarylsulfonium salts and ferrocenes has become technically important. Coatings based on cycloaliphatic epoxy resins have a high gloss and good weather resistance. They adhere to metallic substrates better than the acrylate esters normally used for UV curing but are considerably more expensive.

Glycidyl Esters. These resins were originally developed for electrical applications, but now they are also important in surface protection on account of their good color stability (e.g., Araldite PY 284, Ciba-Geigy). The glycidyl esters of phthalic acid and hexahydrophthalic acid are hot-cured with carboxy-terminated polyesters or polyanhydrides.

Heterocyclic Epoxy Compounds. The technically most important heterocyclic epoxy resin is triglycidyl isocyanurate, obtained by reacting cyanuric acid with epichlorohydrin (Araldite PT 810, Ciba-Geigy; Tepic, Nissan). This trifunctional epoxy resin is combined with carboxy-terminated polyesters to give weather-resistant powder coatings [2.122]–[2.124].

2.10.2. Curing Agents

The most important combinations of epoxy resins and curing agents are summarized in Table 2.6. Depending on their molecular mass, bisphenol A epoxy resins can be cured by polyaddition via their epoxy or hydroxyl groups. Polyamines, polythiols, and polyisocyanates are suitable for room temperature cure. Polyanhydrides, polyphenols, acids, and carboxy-functional polyesters are suitable for hot cure. Epoxy

Table 2.6. The most important epoxy resin—curing agent combinations and their uses

Curing agent	Curing mechanism		Resin type*	M_r	Typical use
Amines and polyamidoamines	via epoxy group	curing at room temperature	liquid	400	two-component systems for heavy-duty corrosion protection and floorings building blocks for chemical modification
Polyamidoamines and amine adducts			solid, type 1 solid, type 2	1 000	industrial maintenance and marine coatings
Latent amines Polyesters			solid, type 3		powder coatings
Phenolic hardeners Amino resins		hot curing	solid, type 4 solid, type 4	2 000 2 000	powder coatings epoxy esters for industrial finishes and can coating
Phenolic resins Amino resins Polyanhydrides			solid, type 6 solid, type 7 solid, type 8	4 000	can coatings and finishes coil coatings
Phenolic resins	via hydroxyl group		solid, type 9		can coatings and finishes
Amino resins Isocyanates				5 000	two-pack polyurethane paints
Isocyanates Phenolic resins Amino resins			high molecular mass epoxy resins	10 000	primers (cold curing) can and coil coatings

* Types 1–9 indicate increasing molecular mass of the respective solid resins.

resins can also be cured by polycondensation with amino resins or phenolic resins. Epoxy resins can be polymerized with catalysts such as tertiary amines, boron trifluoride complexes, ferrocenes, and triarylsulfonium salts.

Polyamines. Aliphatic polyamines cure epoxy resins via their epoxy groups at ambient temperature. Excess amine is generally prereacted with the epoxy resin to form a polyamine adduct. Amines react with monomeric or dimeric fatty acids to form polyamidoamines. Polyamine-adduct-cured epoxy resins have a high chemical resistance. Polyamidoamine-cured epoxy resins exhibit good adhesion and flexibility.

Cycloaliphatic polyamines are less reactive than aliphatic amines, and an accelerator must therefore be used for curing at room temperature (e.g., salicylic acid). Aromatic polyamines are even less reactive than cycloaliphatic amines. Therefore, accelerators must be used to cure aromatic amines with epoxy resins at room temperature [2.125].

Thiols. Thiols have an extremely unpleasant smell, and are only of industrial importance for adhesives and joint groutings. They give a high, permanent flexibility to epoxy resins.

Isocyanates. Whereas polyamines and thiols cure epoxy compounds via their epoxy groups, isocyanates cross-link high molecular mass epoxy resins via their hydroxyl groups to form polyurethanes. The reaction takes place at ambient temperature. These combinations cure more rapidly and at lower temperature than epoxy resins cured with polyamines.

Anhydrides. Polyanhydrides and not monoanhydrides must be used to cure epoxy surface coatings. They are used in powder form for powder coatings and in solution for can coatings; both forms are hot curing. The films have a good acid resistance, and do not impart an undesirable taste to foods.

Acids and Carboxy-Functional Polyesters. Curing of epoxy resins with acids and carboxy-functional polyesters requires heat. Industrially, these systems are most important in the formulation of powder coatings: more than 70% of powder coatings are based on epoxy resins and carboxy-functional polyesters (see also Sections 3.4.2 and 3.4.3).

Polyphenols. Polyphenols react with epoxy resins on heating, but require an accelerator (e.g., tertiary amines, imidazoles). On account of their low color stability, powder coatings based on this combination are not used for decorative purposes, but exclusively for functional purposes where high thermal, mechanical, and chemical resistance is required (e.g., pipe coatings).

Amino Resins. Urea, melamine, and benzoguanamine resins react with high molecular mass epoxy resins on heating. Their hydroxymethyl groups react with one another and with the hydroxyl groups of the epoxy resins to form ether bonds. Such systems are used for coating domestic appliances as well as for packaging.

Phenolic Resins. Phenolic resins react with high molecular mass epoxy resins on heating. Such systems are used as "gold lacquers" to line food containers. The similarly synthesized bisphenol A resols produce colorless coatings with a higher chemical resistance, less odor during cure, and less alteration of the taste of food in contact with the coating. Flexibility is, however, lower than with standard phenolic resins.

Catalytically Curing Compounds. Although tertiary amines can polymerize epoxides even at room temperature, the degree of polymerization is too low to obtain useful coatings. Boron trifluoride complexes polymerize epoxides on heating. Such combinations are sometimes used in powder coatings if high solvent resistance is required.

Ultraviolet curing of epoxy resins has become important. Cycloaliphatic epoxy resins are combined with substances that induce polymerization under the influence of UV radiation or an electron beam. Industrially important products include triarylsulfonium salts (UVE 1014, 1016, General Electric) and arene–ferrocenium compounds (CG 24-061, Ciba-Geigy). To ensure good film flexibility and chemical resistance, polyols should be added. The films should be postcured for 30–120 s at ca. 100°C [2.126].

2.10.3. Chemically Modified Epoxy Resins

Epoxy Resin Esters. Air- or oven-drying esters can be produced by esterification of epoxy resins (M_r 1000–2000) with fatty or oleoresinous

tion and cure [2.164]. Additionally, some release of formaldehyde can take place from cured objects.

The amount of formaldehyde released during the application process is related to the free formaldehyde content in the coating formulation. Loss of formaldehyde from hydroxymethyl groups during storage can raise the free formaldehyde content of a coating formulation.

The release of formaldehyde during the curing process is predominantly the result of dehydroxymethylation reactions. Some of the hydroxymethyl groups are formed during the curing process by hydrolysis of alkoxy groups from moisture in the air. For example, HMMM releases about 0.5–0.8 mol of formaldehyde during the cure process at normal humidity levels. High-imino melamine resins exhibit lower emissions of formaldehyde during cure. Formaldehyde release during cure can be almost eliminated with glycoluril–formaldehyde resin [2.155].

2.13. Phenolic Resins for Coatings
[2.165]–[2.167]

Phenolic resins (i.e., condensation products of phenols and formaldehyde, → Phenolic Resins) are among the oldest synthetic binders, and their first use in paint technology dates back to the early 1920s. Their primary uses have constantly changed since then, and new classes of synthetic binders have become increasingly important.

Initially, phenolic resins attracted a great deal of interest because they appeared to be the first synthetic products that could be used as a substitute for natural resins (rosin, copal resins, shellac). Nowadays attention is mainly focussed on performance and technical-economic competition between the widely differing groups of resins.

The main disadvantage of phenolic resins is their intrinsic yellow to brown color. As a result they cannot be used for colored and white paints. They can only be used for decorative coatings in a few cases (e.g., gold lacquers). Phenolic resins have favorable mechanical properties and a high chemical resistance. Paint systems that are optimally adjusted to the requirement profile can be developed by suitable formulations.

2.13.1. Resols

Resols are phenolic aldehyde resins that undergo self-cross-linking catalyzed with bases or basic salts. Their structure depends on the choice and molar ratios of the raw materials (e.g., phenols and cresols), the solvents, and the type and amount of catalyst used. Resols have free hydroxymethyl groups which can react on heating to form homocondensates. Heterocondensation with other reaction partners is also possible.

Phenolic resins are generally pale yellow to dark brown in color, occasionally of high intensity. In special cases intensely colored resols are used as coloring resins to produce defined shades in coatings (gold lacquers). The products are available in solid (solvent-free) and dissolved form. The choice of solvents is governed by the intended application; resols are generally dissolved in alcohols, glycol ethers, aromatic compounds, or mixtures thereof.

Resols used for coatings generally have a relatively low melting point (ca. 50°C), with the result that solid resins may sinter at high ambient temperatures (ca. 30°C).

Resols suitable for use in paints generally cannot be used as the sole binder because they produce very hard, brittle paint films after stoving. They must therefore be combined with other paint raw materials [e.g., epoxy resins, poly(vinyl butyrals)].

Resols as Sole Binders. Resols are not normally used as the sole binder because of their brittleness. There are cases, however, where flexibility is not important. Uses of phenolic resins as sole binders are restricted to coating rigid constructions (e.g., pipelines and reaction vessels). Several coats are often applied to obtain the desired layer thicknesses. The first coats are cross-linked at relatively low temperature (ca. 170°C) to prevent stress formation within the film. The overall film structure only undergoes complete cross-linking when stoving the last layer. Relatively high stoving temperatures up to 220°C are required for optimum cross-linking.

Resols used alone as thermohardening binders produce coatings with outstanding resistance to chemicals and solvents. Cross-linking takes place primarily via the free hydroxymethyl groups of the resols. The disadvantage of the low flexibility of these coatings has to be borne in mind.

minimum particle size limit is encountered. Lower particle sizes (< 1 μm) can only be obtained with considerable technical effort and expense. Extenders with finer particle sizes are produced synthetically by precipitation. The structure of one and the same extender can be modified by controlling the precipitation conditions. Particularly pure and thus bright extenders can be produced by a suitable choice of starting substances [4.12].

Surface-Treated Extenders. Some extenders tend to form agglomerates during storage, or absorb moisture or additives from the paint mixture. This can be prevented by surface treatment. Stearic acid and its salts are used in large amounts to coat calcium carbonates.

In subsequent developments the aim was to chemically bond the extender and substrate, with the surface-treatment agent acting as a bridging element. Silanes have proved particularly outstanding in this respect and a large number of products with widely varying organic groups (e.g., amino, mercapto, vinyl, and methacrylic groups) are available for this purpose. Such products are usually used to treat kaolins and other silicates.

5. Paint Additives

In addition to resins, solvents, and pigments, paints also contain additives. The additive content is typically between 0.01 and 1 %. Paint additives are used to prevent defects in the coating (e.g., foam bubbles, poor leveling, flocculation, sedimentation) or to impart specific properties to the paint (e.g., better slip, flame retardance, UV stability) that are otherwise difficult to achieve.

Such products were formerly termed "auxiliaries" and were often only used to correct a paint batch that did not comply with the required specifications and showed some defects. Nowadays additives are already taken into consideration when a new paint formulation is created; they form an essential constituent of the coating. In view of the increasingly stringent quality and environmental requirements for the production and use of coatings, high-quality paint systems are almost always formulated with additives.

Many effects can be achieved with additives, and not all of their, in some cases, very specific

uses can be discussed here. Information on paint additives and their mode of performance is given in the literature and company brochures. There is very little comprehensive literature on additives [5.1], [5.2]. The physical and chemical principles of paint production and application are helpful in understanding their mode of action [5.3], [5.4]. A large number of paint additives are listed according to areas of use in special tables [5.5]–[5.7].

Additives may be classified in the following groups:

1) Defoamers
2) Wetting and dispersing additives
3) Surface additives
4) Rheology additives
5) Driers and catalysts
6) Preservatives
7) Light stabilizers
8) Corrosion inhibitors

This subdivision is by no means exhaustive. Individual products cannot always be assigned to one of these groups because one additive may simultaneously influence a combination of paint properties. Additionally it is sometimes difficult to draw the line between additives and other paint ingredients (e.g., resins, pigments, extenders, and solvents) when these materials are used in an additive-like manner.

5.1. Defoamers

Although foam may occur as an interfering factor during paint production, most problems arise when it causes surface defects during the application process.

Liquid foams are a fine distribution of a gas (normally air) in a liquid. Thin films of liquid (the lamellae) separate the gas bubbles from one another and the gas—liquid interfacial area is quite high. For a detailed description, see → Foams and Foam Control.

Defoamers (antifoaming additives) are liquids with a low surface tension which have to satisfy three conditions:

1) They must be virtually insoluble in the medium to be defoamed
2) They must have a positive penetration coefficient E
3) They must have a positive spreading coefficient S

$$E = \sigma_L - \sigma_D + \sigma_{L/D} > 0$$
$$S = \sigma_L - \sigma_D - \sigma_{L/D} > 0$$

σ_L = surface tension of the liquid phase
σ_D = surface tension of the defoamer
$\sigma_{L/D}$ = interfacial tension between the liquid and the defoamer

If both E and S are positive, the defoamer penetrates into the foam lamella and spreads across the surface. This creates interfacial tension differences that destabilize the lamellae and cause the foam to collapse. In simple terms it can be said that defoamers act because of their controlled incompatibility with the paint system. If a defoamer is too compatible its defoaming effect is not sufficient, if it is too incompatible film defects occur (e.g., gloss reduction, formation of craters).

For *waterborne paint systems* (especially emulsions used for decorative purposes) defoamers based on mineral oils are often used (→ Foams and Foam Control, A11, pp. 480–482). In addition to the mineral oil as carrier, these products contain finely dispersed hydrophobic particles (e.g., silica, metal stearates, polyureas) as defoaming components. A small amount of silicone is sometimes included to intensify the defoaming action. For high-quality waterborne coatings in industrial applications, defoamers are used that contain hydrophobic silicone oils as the principal defoaming component instead of mineral oils. They have a better defoaming effect, but are more expensive. In most cases silicone defoamers do not cause the gloss reduction that is often observed with mineral oil products.

Silicones are also the predominant defoamer components in *solventborne coatings*. Products with a correct balance of compatibility and incompatibility can be synthesized by selectively modifying the silicone backbone with polyether or alkyl chains.

$$(CH_3)_3Si-O-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ R \\ | \\ O \\ | \\ \left[\begin{array}{c} CH_3 \\ | \\ CH-R \\ | \\ O \\ | \\ R \end{array}\right]_z \end{array}\right]-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ (CH_2)_n \\ | \\ CH_3 \end{array}\right]_r-Si(CH_3)_3$$
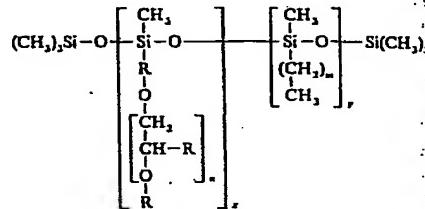
Silicone-free defoamers based on other incompatible polymers (e.g., acrylates and acrylic copolymers) are also commercially available.

Commercial products include Agitan (Münzing); Airex, Foamex (Tego); Byk-020, -052 (Byk); Colloid 681 F (Colloids); Dehydran (Henkel); Disparlon OX-710 (Kusumoto); and Drewplus L-475 (Drew).

5.2. Wetting and Dispersing Additives

In the production of pigmented paints, the pigment particles must be distributed as uniformly and as finely as possible in the liquid phase (see Section 7.2.2). The pigment agglomerates must first be wetted by the binder solution
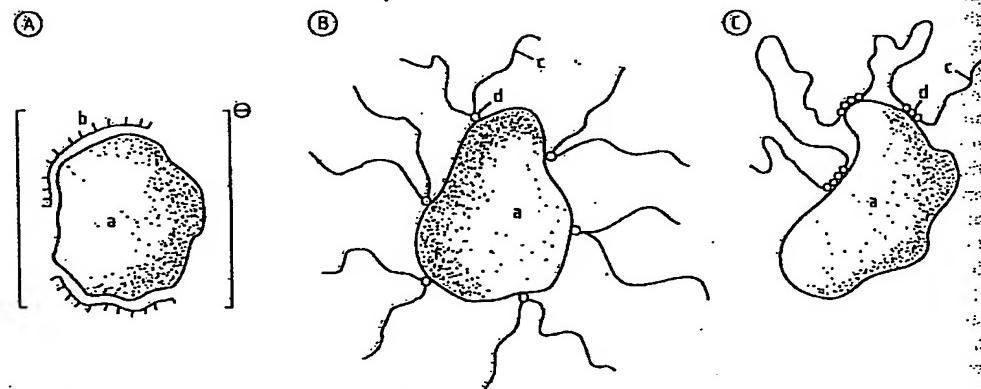

Figure 5.1. Stabilization of pigment dispersions
A) Electrostatic charge repulsion induced by polyelectrolytes; B) Steric hindrance through low molecular mass dispersing additives; C) Steric hindrance through polymeric dispersing additives
a) Pigment particle; b) Polyelectrolyte; c) Molecular structure causing steric hindrance; d) Pigment-affinic group

This process mainly depends on the chemical nature of the pigments and binders and can be accelerated by using *wetting additives*. Wetting additives are materials of low molecular mass with a typical polar–nonpolar surfactant structure; they reduce the interfacial tension between the binder solution and the pigment surface.

After the agglomerates have been broken down into smaller particles by impact and shear forces (grinding, milling), the pigment dispersion must be stabilized to avoid reformation of larger pigment clusters by flocculation. *Dispersing additives* are stabilizing substances that are adsorbed onto the pigment surface via pigment-affinic groups (anchor groups with a high affinity for the pigment surface) and establish repulsive forces between individual pigment particles. Stabilization is achieved either via electrostatic charge repulsion (Fig. 5.1 A) or via steric hindrance due to molecular structures that project from the pigment surface into the binder solution (Fig. 5.1 B and C). The first mechanism is prevalent in waterborne emulsion systems, the latter predominates in solventborne paints. In coatings with water-soluble resins both mechanisms are equally important.

Good adsorption of the additive to the pigment surface is necessary for efficient stabilization. Problems may arise in this respect with many organic pigments because of their highly nonpolar surface. A new group of dispersing additives has therefore been developed recently. These polymeric wetting and dispersing additives can stabilize such difficult pigments by virtue of their macromolecular structure and the large number of pigment-affinic groups (Fig. 5.1 C).

Wetting and dispersing additives can also solve flooding and floating problems. Since most paints contain more than one pigment, the pigments often segregate in the paint film during drying. Nonuniform pigment distribution within the film surface is termed *floating* [formation of Bénard cells (Fig. 5.2 A) and streaks]. In *flooding* the surface is uniformly colored, concentration and thus shade differences occur only perpendicular to the surface; this phenomenon only becomes evident in the rub-out test (Fig. 5.2 B). In this test, after a short drying period part of the wet paint film is rubbed with the finger until almost dry (i.e., until it starts to become tacky). This treatment distributes the pigments evenly in the paint film and segregation is not possible. A color difference detected between the rubbed
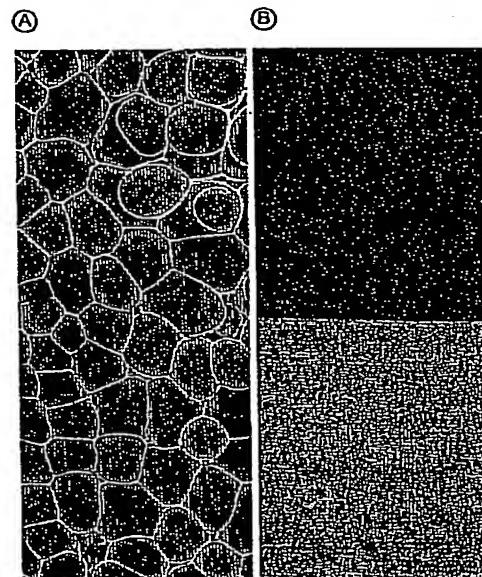
Figure 5.2. Uneven pigment distribution (color differences) due to flooding and floating
A) Bénard cells; B) Rub-out test

section and the untouched area indicates flooding.

Flooding and floating are caused by local eddies in the drying paint film. The pigment particles undergo eddy motion and if they differ in mobility, they can become separated from one another. The mobility of the pigments depends on density, size, and the strength of their interactions with the binder molecules. Additives can minimize mobility differences between different pigments by controlling these pigment–binder interactions and thereby prevent flooding and floating.

Another way of avoiding flooding and floating is to prevent the separation of the pigments by coflocculation. Additives that work in this way are known as controlled flocculating additives (Fig. 5.3). They form bridges between pigment particles and thus build up flocculates. Size and stability of the flocculates are controlled by the additive. This method is, however, not ideal for high-quality topcoats because flocculation may reduce gloss and impair other paint proper-
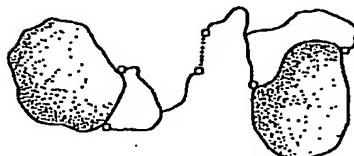
Figure 5.3. Controlled flocculation

ties (e.g., hiding power, color strength, transparency). Controlled flocculation also changes the rheology of the paint system (see Section 5.6). Wetting and dispersing additives with such properties are often used in combination with other rheological additives. They enhance the action of the rheological additives, often synergistically, and problems such as sagging and settling can be overcome. In the case of settling, the presence of an additive layer on the pigment surface prevents the formation of hard sediment which would be difficult to stir in again. Instead any settled material formed is soft and easy to incorporate again. *Antisettling additives* generally increase the low shear viscosity to improve suspension of the pigment particles and avoid the formation of hard sediments.

Commercial products include Anti-Terra, Disperbyk-161 (Byk); Borchigen ND (Borchers); Ser-Ad FA 601 (Servo); Solsperse (ICI); Surfynol (Air Products); Tamol, Triton (Rohm & Haas); and Texaphor (Henkel).

5.3. Surface Additives

Many surface defects can be explained by differences in interfacial tension. Poor substrate wetting, for example, must be expected if the paint has a higher surface tension than the substrate to be coated. When spray dust or solid dust particles fall onto a freshly coated surface, *craters* are formed if the deposited droplets or particles have a lower surface tension than the surrounding paint material. Craters are also formed if the surface to be coated is locally contaminated with substances having a very low surface tension (e.g., oils) and the surface tension of the paint is too high to wet these contaminated areas.

Surface tension differences may also develop within the paint itself: during drying the solvent evaporates and this change in composition also alters the surface tension. Even slight surface tension differences lead to the formation of Bé-

nard cells which may result in visible surface defects such as *orange peel* and *air draught sensitivity*.

In general, surface tension differences lead to material transport in the liquid paint film from the region of lower surface tension to that of higher surface tension. This movement is responsible for the above-mentioned defects. Other phenomena such as fat edges, picture framing, and ghosting can be explained in a similar way.

Silicone additives (mainly organically modified methylalkyl polysiloxanes) lower the surface tension of coatings and minimize surface tension differences.

$$(CH_3)_3Si-O-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ Organic \\ modification \end{array}\right]_n-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ Alkyl \end{array}\right]_r-Si(CH_3)_3$$
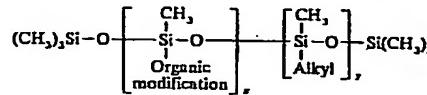
They are therefore ideal for solving the problems described above. Organic modification of the silicone (polyether and polyester chains, aromatic groups) serves to adjust the compatibility with the paint system. The alkyl groups have a strong influence on the surface tension: methyl groups give very low surface tension, longer alkyl chains give higher values.

Silicone additives also improve the *slip properties* of the dried coating which then exhibits improved blocking and scratch resistances. Similar effects can be achieved with waxes which can have an additional flattening effect.

Poor *leveling* is also considered a surface defect. The leveling properties of a coating depend on many factors. Silicones influence the surface structure by suppressing eddy motion during drying. Acrylate copolymers are also used for the same purpose. They are incompatible with the paint system and accumulate at the surface. They also have a stabilizing effect on the surface but do not lower the surface tension as strongly as silicones. Silicone and acrylate flow additives are also known as *surface flow control additives* (SFCA). Leveling also depends highly on paint rheology which can be modified by using special solvent blends. Finally it should be remembered that wetting and dispersing additives can also alter the rheology and thus influence leveling.

Commercial products include Baysilone (Bayer); Byk 306, -310 (Byk); Disparlon 1980 (Kusumoto); Dow 11 Additive (Dow Corning); KP-321 (Shin-etsu); Perenol (Henkel); SF 69 (General Electric); Siliconöl AK35 (Wacker); Silwet (Union Carbide); Slip-Ayd (Daniel); Tegoglide (Tego); and Worlee Add 315 (Worlee).

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5.4. Driers and Catalysts

Driers (siccatives) are used in paint systems that dry at ambient temperature by oxidation processes. They accelerate the drying process by catalyzing the autoxidation of the resin. Driers are in general organometallic compounds (metallic soaps of monocarboxylic acids with 8–11 carbon atoms), the metal being the active part. Cobalt and manganese (primary or surface driers), lead, calcium, zinc, zirconium, and barium (secondary or through driers) are mainly used (→ Metallic Soaps). In practive, mixtures of metallic soaps are commonly used to obtain the optimum ratio of through drying to surface drying. Secondary driers cannot be used on their own, they always have to be combined with primary driers.

Driers can cause skin formation during paint storage, particularly if the can or container has been opened. Oximes or alkylphenols are added as *antiskinning additives*. They block the action of the driers in the can, but at the correct dosage do not prolong the drying time of the applied paint film due to their volatility.

The curing of coatings that are cross-linked by other chemical reactions can be accelerated with *catalysts*. Acid catalysts are the most important and are used for a large number of stoving enamels and force-dried, acid-curing wood paints. They are mostly sulfonic acids of widely varying structure, often blocked with amines to allow formulation of storage-stable paints. The use of a catalyst can lower the stoving time and/or stoving temperature to save energy or to permit the coating of temperature-sensitive substrates.

Catalysts also include accelerators for two-pack polyurethane paints (e.g., tin and zinc compounds, tertiary amines) and initiators for unsaturated polyester resins that act as radical-forming agents.

Commercial products include Additol XW 335 (Hoechst); Byk Catalysts (Byk); Cycat (Dyno Cyanamid); Dabco, Polycat (Air Products); K-cure, Nacure (King); Manosec Cobalt 6% (Manchem); Metatin Kat (Acima); Nuodex Cobalt 6% (Nuodex); and Troykyd Cobalt 6% (Troy).

5.5. Preservatives

Preservatives have to be subdivided into in-can preservatives and in-film preservatives. *In-can preservatives* protect waterborne paint systems against contamination by microorganisms during production, transportation, and storage. *In-film preservation* is aimed at preventing the growth of bacteria, fungi, and algae on the applied paint film and is the more demanding task. A special area of use is the protection of wood against biodegradation by putrefactive fungi and insects. Antifouling additives for underwater coatings that are intended to prevent marine growth are also included in this category (see also Section 11.4).

Preservative measures are governed by the intended use of the coating. There are no universal additives on account of the large number of possible types of damage; combination products containing several active ingredients are available and often used. Organomercury compounds, chlorinated phenols, and organotin compounds were often used, but these environmentally harmful products are now being replaced more and more by metal-free organic substances, mainly nitrogen-containing heterocycles.

Commercial products include Mergal (Riedel de Haen); Metatin, Tractex (Acima); Nopcocide (Henkel); Nuodex Fungitrol (Nuodex); Preventol (Bayer); Proxel (ICI); and Troysan (Troy).

5.6. Rheology Additives

The flow properties of paints can be modified with rheology additives. This is important for obtaining optimum application behavior of the paint material, i.e., good leveling and no sagging at the desired film thickness. Paint rheology also plays a role in storage stability (settling, see Section 5.2).

Thickeners, mainly cellulose derivatives (e.g., methyl cellulose, ethylhydroxypropyl cellulose) or polyacrylates, are generally used in emulsion paints. Recently polyurethane thickeners (associative thickeners) with more favorable leveling properties are also increasingly used.

A large number of rheological additives for solventborne systems are commercially available. Hydrogenated castor oils, pyrogenic silica, and modified montmorillonite clays (organoclays, e.g., bentonite) are preferred.

The rheological action of the above additives is based on the fact that they form three-dimensional networks in the paint. These lattice structures are destroyed by shear forces but are re-
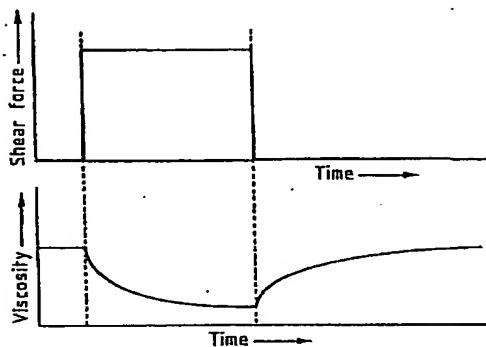
Figure 5.4. Thixotropy: viscosity is shear-force-dependent and time-dependent

stored when the forces are removed. This recovery is not, however, immediate. The rising viscosity initially allows leveling of the surface but subsequently prevents sagging. This time-dependent change in viscosity is known as thixotropy (Fig. 5.4). In paints thixotropy is more desirable than purely pseudoplastic flow behavior because it allows a compromise between sagging and leveling.

Commercial products include Acrysol RM-4 (Rohm & Haas); Aerosil 200 (Degussa); Bentone, Thixatrol (NL); Talen 7200-20 (Kyoeisha); and Tixogel (Südchemie).

5.7. Light Stabilizers

High-quality industrial coatings, especially automotive finishes, are subjected to severe weathering in exterior applications. In two-coat metallic coatings, exposure to UV light, oxygen, moisture, and atmospheric pollution causes decomposition of the polymer material in the automotive finishes. This decomposition results in loss of gloss, crack formation, color changes, and delamination phenomena [5.8].

High-energy UV light is particularly detrimental because each polymer material can be damaged particularly easily at one or more wavelengths in the UV range. Light stabilization is therefore essential [5.9].

Methods of Stabilization. Two stabilization methods have been adopted industrially [5.10], [5.11]:

1) Competitive UV absorption by UV absorbers in the wavelength range 290–350 nm.
2) Trapping of the radicals formed during polymer degradation by radical scavengers (hindered amine light stabilizers, HALS).

In two-coat metallic paints, the basecoat is protected against color change and photochemical decomposition (which leads to delamination) by the filter effect of the UV absorber that is added to the clearcoat; UV absorbers cannot trap radicals. Hindered amine light stabilizers do not absorb in the UV region, but trap radicals already formed, and are mainly responsible for the gloss retention and prevention of crack formation in paints. Optimum protection against decomposition phenomena in the coating is achieved by using a combination of both stabilization methods.

UV Absorbers. Four different classes of UV absorbers are shown below:
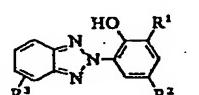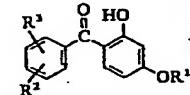
Hydroxyphenylbenzotriazoles   Hydroxybenzophenones
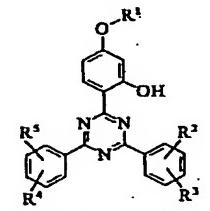
Hydroxyphenyl-S-triazines   Oxalic anilides
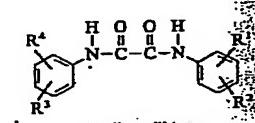
The hydroxyphenylbenzotriazoles are the most important. They absorb the damaging UV light and rapidly convert it into harmless heat (keto enol tautomerism) [5.11].

The action of all UV absorbers depends on the Lambert–Beer law, and the absorption properties of the UV absorber. The further the absorption edge extends into the near UV region, the more UV light can be filtered out. Of the four UV absorber classes shown above, the hydroxyphenylbenzotriazoles have the broadest absorption band [5.8], [5.12]. In addition to thermal stability [5.12] and stability to extraction with water or organic solvents, photochemical stability is important [5.13]–[5.15]. Ultraviolet reflection spectroscopy can be used to establish

whether the employed UV absorber is still effective, even after several years' external weathering [5.16]. The hydroxyphenylbenzotriazoles have a much higher photochemical resistance than oxalic anilides and hydroxybenzophenones [5.8], [5.12], [5.17].

Radical Scavengers (Sterically Hindered Amines). Two typical sterically hindered amines (HALS = Hindered Amine Light Stabilizer) follow:

$$\left[R-N \left\langle \begin{array}{c} H_3C \; CH_3 \\ \\ H_3C \; CH_3 \end{array} \right\rangle \begin{array}{c} H \; O \\ | \; \| \\ O-C-(CH_2)_4 \end{array} \right]_2$$

HALS I, R = CH_3 $pK_b \approx 5.5$
HALS II, R = O-i-C_8H_{17} $pK_b \approx 10$
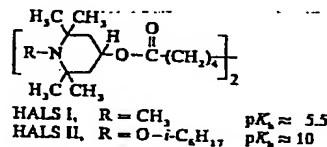
The tetramethylpiperidine group is responsible for the stabilizing action. Different substituents on the nitrogen atom result in different pK_b values, which are important in the area of use of the products. HALS I, bis(1,2,2,6,6-pentamethyl-4-piperidinyl) ester of decanedioic acid [415526-26-7], is used in systems that are not catalyzed by strong acids (interaction of the acid with the basic nitrogen atom). HALS II, bis(2,2,6,6-tetramethyl-1-isooctyloxy-4-piperidinyl) ester of dec-
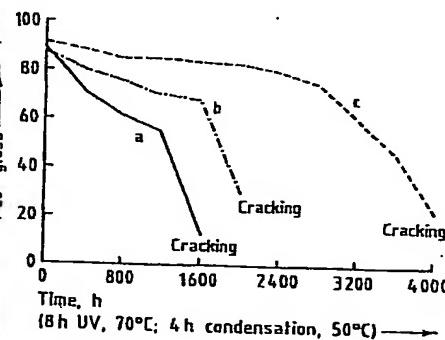
Figure 5.5. Accelerated weathering of an acid-catalyzed two-coat metallic coating in an UVCON apparatus (Atlas Corp.)
Clearcoat: high-solids acrylic—melamine; Basecoat: high-solids acrylic—melamine, silver metallic; Bake: 120°C, 30 min; Benzotriazole II: 3-(2H-benzotriazole-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyoctyl benzenepropanoate [84268-23-5]
a) Unstabilized; b) 2.5% Benzotriazole II; c) 1.5% Benzotriazole II and 1% HALS II (percentage relative to binder solids)

anedioic acid [122586-52-1], was developed for acid-catalyzed systems because it does not undergo undesirable interactions with acid catalysts.

The mode of action (Densiov cycle) of HALS (as deduced from investigations on polyolefins) follows (P = polymer) [5.11], [5.18]:

$$\rangle NO\cdot + P\cdot \longrightarrow \rangle NOP$$

$$\rangle NOP + PO_2\cdot \longrightarrow \rangle NO\cdot + POOP$$
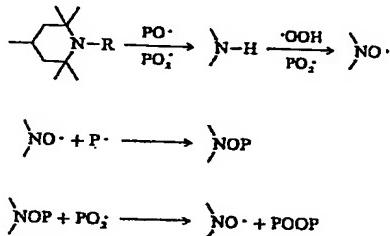
The formation of nitroxyl radicals $\rangle NO\cdot$ is essential for stabilization since the concentration of harmful peroxy radicals falls sharply in their presence [5.19].

Light stabilizers are tested under artificial weathering conditions (accelerated weathering) and under outdoor weathering (Florida, 5° South, black box, not heated) [5.17]. Figure 5.5 and Table 5.1 illustrate the influence of light protection agents on gloss retention and crack formation in two-coat metallic coatings.

Table 5.1. Outdoor exposure of a two-coat metallic coating[a]

Light stabilizer	20° gloss after n years Florida				
	$n=0$	$n=2$	$n=4$	$n=6$	$n=8$
Unstabilized[b]	93	45			
1% Benzotriazole I[c]	94	71	58		
1% Benzotriazole I and 1% HALS I	94	70	67	56	50

[a] Clearcoat, acrylic—melamine; basecoat, polyester—cellulose, acetobutyrate—melamine, silver metallic; bake: 130°C, 30 min; exposure: Florida, 5° South, black box unheated; percentage of light stabilizer relative to binder solids; benzotriazole I, 2-(2H-benzotriazole-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol [70321-86-7]. [b] Cracking after 2.25 years. [c] Cracking after 5.5 years.

5.8. Corrosion Inhibitors

To obtain a coating with good corrosion protection, *anticorrosion pigments* have to be used (e.g., red lead, zinc chromate, zinc phosphate,

→ Pigments, Inorganic) and/or the paint must act as a barrier against the agressive media.

Corrosive inhibitors do not have pigment properties because they are soluble in the paint system and are not colored. They inhibit corrosion processes on ferrous surfaces (in the can and on the substrate to be coated). Typical examples are flash-rust inhibitors such as sodium nitrite and sodium benzoate for waterborne systems. Nitrogen-containing organic substances, tannin derivatives, and chelating compounds are still in industrial use. Some metal complexes of nitrogen-containing organics exhibit very good performance in combination with zinc phosphate.

Commercial products include Busan 11-M1 (Buckman); Raybo 60 NoRust (Raybo); Ser-Ad FA179 (Servo); and Sicorin RZ (BASF).

5.9. Use and Testing of Additives

Additives are generally used in very small amounts (≤1% of total formulation) and correct dosage is extremely important for optimum effectiveness and also to avoid undesirable side effects. The dosage has to be determined in test series.

Many additives can be incorporated relatively easily into the paint system during or after the last phase of production (let down). In some cases, however (e.g., with many rheological additives), certain incorporation conditions have to be observed. Wetting and dispersing additives, for example, always have to be present in the millbase to achieve the desired results.

Ideally, the effectiveness of an additive should be checked in the complete formulation and under conditions as close as possible to those prevailing in practice. Checking a defoamer just in the binder system, for example, can only be regarded as a preliminary test, because the behavior in the complete formulation may differ substantially.

Many defects that are to be eliminated by the use of additives are also influenced by the substrate to be coated and the application method. Differences between additives can be established in simple laboratory tests. However the final composition of a specific formulation must take into account as many application parameters as possible (e.g., the state of substrate, application method, and drying conditions).

In most cases additives influence not just one property of the coating. They may also have undesirable or beneficial side effects. Additives are not "magical" products but need to be used rationally and carefully to provide the desired satisfactory results. As detailed and complete a knowledge as possible of the mechanism of action of the products, their possible effects and side effects, their limitations, and the underlying causes of paint defects are certainly helpful, but due to the complexity of paints and coatings empirical knowledge is indispensible.

6. Paint Removal

The nature, condition, and quality of the paint and substrate are important in paint removal. The paint binder plays a decisive role in paint dissolution; the substrate influences the choice of paint removal method. Various chemical and physical methods exist for removing paint from different substrates (metals, wood, and mineral substrates) [6.1], [6.2].

6.1. Paint Removal from Metals

6.1.1. Chemical Paint Removal

Paint layers can be stripped (dissolved) or degraded with chemicals [6.3]. Paint dissolution is performed with organic solvents, whose action is assisted by surfactants. Paint binders can be degraded with strong alkali or acid. Depending on their use, paint removers may also contain cosolvents, activators (acid or alkali), wetting agents, emulsifiers, evaporation retarders, corrosion inhibitors, and thickening agents. The efficiency of paint removers is improved by increasing the temperature; the paint removal time can be substantially shortened by raising the temperature of the bath (2–6 h at 20–95 °C).

The *advantages* of chemical paint removal are that it can be used for almost all types of paints, geometries, and heat-sensitive items. Investment costs are low and waste air does not cause serious environmental problems. The *disadvantages* are the relatively long removal time and formation of a paint slurry which leads to higher waste disposal costs.

Hot Alkaline Paint Removal Baths. Paint removal takes place in hot, aqueous, alkaline baths